

THE EFFECT OF SODIUM OLEATE ON THE ABSORPTION OF AMMONIA
BY WATER IN A SPRAY TYPE COLUMN

A THESIS

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ABSTRACT

The purpose of the investigation was to study the effect of surface tension and the concentration of an added surface active agent, sodium oleate, upon the over-all gas film coefficient for the absorption of ammonia from various air and ammonia mixtures passed through a modified spray column at atmospheric pressure and room temperature, using water as the absorbent.

The previous investigations on this topic were reviewed and the structure of liquid surface films was discussed. The Gibbs absorption equation was discussed and the restrictions on its use were presented.

The equipment consisted of a 7.56 inch glass column four feet high, gas and liquid distributors, calibrated rotameters for the measurement of the gas and liquid flow rates, an ammonia cylinder, an air source, a liquid reservoir, and various valves and fittings for the regulation of flow rates and for sample removal.

The over-all gas film coefficients for the absorption of ammonia from air and ammonia mixtures, varying from one to five per cent ammonia at a liquid rate of 0.5 pounds per minute and ammonia flow rates varying from 0.147×10^{-3} to 2.058×10^{-3} pound moles per

minute, were calculated. The surface tension of the aqueous phase was varied from 72.8 to 29.0 dynes per centimeter by the addition of sodium oleate.

When the logarithm of the over-all gas film coefficient was plotted against the logarithm of the total gas rate in cubic feet per minute a straight line which could be expressed algebraically by the following equation was obtained:

$$K_G = 0.76 u^{0.258}$$

where: K_G is the over-all gas film coefficient in pound moles per hour per square foot per atmosphere

u is the total gas rate in cubic feet per minute at one atmosphere and 80 degrees Fahrenheit

From the data obtained in the experimental study the following conclusions were drawn:

1. The presence of sodium oleate in the liquid phase in no way affected the over-all gas film coefficient.

2. The decrease in surface tension obtained by the use of the sodium oleate was responsible for increased absorption of the ammonia, but this effect was due to the increase in surface area.

CHAPTER I

INTRODUCTION

Absorption, as a unit operation in Chemical Engineering, has come to mean the process of transferring mass from a gaseous phase into a liquid phase. Two other closely allied processes are stripping, which is the reverse of absorption, and adsorption, in which the mass transfer ends at the interface of the two phases.

Absorption processes are commonly used in industry for the removal of various components of gaseous streams. An example of this process would be the removal of ammonia from a flue gas where the recovery would be both economically feasible for re-use in the process and necessary to prevent air pollution.

There are several unit operations that involve mass transfer between phases, namely absorption, adsorption, distillation, and extraction. These processes possess essentially the same mechanism of interphase mass transfer and it is felt, that since all of these unit operations are of importance in industry, a thorough study of interphase mass transfer is necessary to understand these processes.

Gas absorption has been a basic process since the advent of the large scale chemical industry. Much study and effort has been employed to better understand and predict results obtained from various types of absorption equipment. Continuous processes are normally preferred to batch operations because of economy and ease of control. The most

common types of continuous absorption apparatus are packed columns, plate columns, wetted wall columns and spray columns. The selection of the type of column is usually determined by economic factors. The process which can provide the most intimate mixing of the gas and liquid streams will necessarily perform the most complete separation up to, of course, the limit imposed by equilibrium of the two phases.

In all of the literature treating absorption problems, there has been comparatively little study of the influence of surface tension and the concentration of an added surface active agent on the absorption rate of a gas in liquid.

Surface films.--Since this investigation involves mass transfer through surface films, it seems in order to present some of the postulates and theories regarding the effect of surface active agents in these films.

The basic relation used to determine the concentration of a surface active agent in the liquid surface was the adsorption equation first derived by J. W. Gibbs (1). This equation is:

$$\Gamma = - (c/RT) (\partial \gamma / \partial c) \quad (1)$$

where: Γ is the excess of the surface active agent in the surface of the solution

c is the concentration of the surface active agent in the bulk of the solution

T is the temperature

γ is the surface tension of the solution

R is the gas constant

(1) Gibbs, J. W., Collected Works of J. W. Gibbs. New York: Longmans, Green and Company, 1931, Vol. I, p. 219.

The assumption used by Gibbs in the derivation of the adsorption equation limits its application to an isothermal, isobaric system in a state of static equilibrium. Further limitations are the postulations of a plane surface of negligible thickness, generally referred to as the Gibbs surface or film, and of a dilute solution where the concentration of the solute is proportional to the mole fraction of the solute in the solution or the assumption of unit fugacity and activity.

Langmuir (2) from his study of the films of insoluble substances upon water, concluded that the film was but one molecule thick and that the molecules were definitely oriented. He proposed that in such cases, for both soluble and insoluble substances and for pure liquids, the Gibbs film may be regarded as but one molecule thick and consisting of pure solute molecules which lower the surface tension of the solution.

Lord Rayleigh (3), from his studies of a surface film of oleic acid spread upon water, suggested that the film consisted of a single layer of molecules which could be regarded as floating objects.

Rideal (4) states, that when using various concentrations of a single surface active agent in water, the Gibbs film appears to be unimolecular in character. He further states that the area per molecule on the surface is increased or decreased in inverse proportion to the change in concentration of the agent in the solution. Rideal explains this by the proposal that the end of the chain of a molecule of the

(2) Langmuir, I., J. Am. Chem. Soc. 39, 1848 (1917).

(3) Rayleigh, Lord J. W., Proc. Royal Soc. 47, 364 (1890).

(4) Rideal, E. K., Surface Chemistry. Cambridge, England: The University Press, 1930, p. 83.

agent is dissolved in the solvent and the normally insoluble hydrocarbon chain extends above the surface of the liquid, thus when the agent is more concentrated in the solution, the molecules are more closely packed and the corresponding surface area per molecule is lessened. He concludes that in this arrangement, there is no reason to suppose that the molecules would lie flat upon the surface and arrange themselves in polymolecular layers. However, this evidence is by no means conclusive for very high concentrations of the agents. Rideal further says that although most interphase mass transfers take place at great speed, as in the vaporization and condensation of water at the normal boiling point, the life of a molecule on the surface is probably long enough to permit such adjustments as orientation requires.

Many additional investigators have concluded that the surface film is of one molecule thickness and consists of oriented or partially oriented molecules.

This brief presentation of the basic theories accepted in the field of surface phenomena should be sufficient to establish the background for this investigation. Reference will be made to these points when the evaluation of the results of the investigation is presented.

Surface tension in gas absorption.--The investigations reported in the literature on this subject do not agree on the effects of the surface tension of the liquid phase on the rate of interphase transfer.

Riou and co-workers (5,6) in their study of the absorption of

(5) Riou, P., and L. Lortie, Comptes Rendus 186, 1543 (1928).

(6) Riou, P., and P. Cartie, Comptes Rendus 186, 1727 (1928).

carbon dioxide gas in water solutions of carbon dioxide containing small amounts of various surface active agents, reported that the rate of absorption decreased rapidly as the concentration of the added agent was increased. They concluded that the effect could not be due to viscosity because of the low concentrations of the agents added and that it must be due to a catalytic effect.

Killefer (7) made a study similar to that of Riou and found that even in low concentrations of agents the slope of the absorption curve was greatly increased in a packed column, indicating that the rate of absorption was increased when these agents were present. However, he did not relate this increase in any manner to a catalytic action of the added surface active agents.

Smith and Quinn (8) performed a similar investigation with the systems used by Riou and Killefer and decided that the effect observed on the absorption rate must be attributed to the change in the surface tension of the solution.

Rennolds (9) concluded from the results of his experimental study on desorption in a packed column using various wetting agents that the rate of absorption in systems which include one of these agents is lowered only when the liquid film is controlling. Similar observations have been made by other investigators including Sherwood and his

(7) Killefer, D. H., Ind. & Eng. Chem. 29, 1293 (1937).

(8) Smith, J. H., and E. L. Quinn, Ind. & Eng. Chem. 33, 1129 (1941).

(9) Rennolds, J. H., Jr., S. M. Thesis, M. I. T., 1939.

co-workers (10,11,12) who propose that the decrease in the rate of absorption is due to the presence of the large molecules of the surface active agents upon the liquid surface which impede the movement of the diffusing molecules in the film, thus increasing the resistance of the liquid film to diffusion.

Pozin (13,14) investigated the absorption of ammonia by solutions of acetic, succinic, nitric, and hydrochloric acids. He reported that the rate of absorption is in no way related to the surface tension of the absorbing solutions.

Ternovskaya and Belopolskii (15,16) studied the absorption of sulfur dioxide in a wetted wall column by water containing small amounts of surface active agents such as merzalyat, sulfonol or nekale. They found that the rate of absorption decreased rapidly at first then flattened out as the concentration of the surface active agent increased, except for nekale which exhibited a minimum before the rate became relatively independent of the concentration. They concluded that this was due to

(10) Sherwood, T. K., and F. A. L. Holloway, Trans. Am. Inst. Chem. Engrs. 36, 611 (1940).

(11) Sherwood, T. K., and F. J. Jenny, Ind. & Eng. Chem. 27, 265 (1935).

(12) Sherwood, T. K., and F. A. L. Holloway, Ind. & Eng. Chem. 30, 765 (1938).

(13) Pozin, M. E., J. Applied Chem. (USSR) 20, 344 (1947).

(14) Ibid., p. 754.

(15) Ternovskaya, A. N., and A. P. Beloposkii, J. Phys. Chem. (USSR) 24, 43 (1950).

(16) Ibid., p. 981.

a change in the hydrodynamic conditions--wave motion and ripple formation--caused by the addition of the surface active substances. Grimley (17) came to the same conclusion.

In the discussion of a paper by Sherwood, Evans and Langcor (18) on extraction in spray and packed columns, Johnstone (19) stated that he had observed that the addition of a very small amount of tergitol decreased the extraction of acetic acid from ether by water to one-third of that obtained in its absence. Johnstone believed this to be caused by the change in interfacial tension.

Purpose of the investigation.--The purpose of this investigation was to study the effect of surface tension and the concentration of an added surface active agent, sodium oleate, upon the over-all gas film coefficient for the absorption of ammonia from various ammonia and air mixtures passed through a modified spray column at atmospheric pressure and room temperature using water as the absorbent.

This investigation was conducted with a constant liquid flow rate and with various gas flow rates, gas compositions and surface active agent concentrations. As many restrictions as possible were placed upon the system in order to eliminate experimental error so that the effect of the surface active agent could be definitely established.

(17) Grimley, S. S., Trans. Inst. Chem. Engrs. (London) 23, 228 (1945).

(18) Sherwood, T. K., J. E. Evans, and J. V. A. Langcor, Trans. Am. Inst. Chem. Engrs. 35, 597 (1939).

(19) Johnstone, H. F., Chem. & Met. Eng. 49, 78 (1942) Vol. 5.

CHAPTER II

EXPERIMENTAL EQUIPMENT AND MATERIALS

Equipment.--The experimental equipment consisted essentially of a glass column, a liquid reservoir, a liquid pump, an air compressor, a cylinder of ammonia, and various devices for controlling and metering the liquid and gaseous streams. Schematic diagrams and photographs of the construction and layout of experimental equipment are shown in Figures 1 through 8 inclusive.

The column used in this investigation was a 7.56 inch inside diameter laboratory glass cylinder, four feet high mounted in a supporting structure as shown in Figures 4 and 5. The glass column was seated on a plastic adaptor placed on the column bottom assembly and was sealed with a heavy coat of grease.

The air system, as shown in Figures 1 and 3, was supplied with air by the central laboratory compressor at a pressure varying from 90 to 110 psig. A liquid trap was located in the line to remove water condensed in the main air supply line. The pressure was then reduced by two spring activated diaphragm type pressure regulators in series to the approximate operating pressure of 10 psig. A section of two inch standard pipe packed loosely with glass wool served as an air filter to remove any small particles of entrained material. The air stream was metered through a previously calibrated rotameter. Pressure was maintained in the rotameter by control of the downstream pressure at the downstream

pressure control needle valves and by adjustment of the flow rate to the rotameter by the inlet flow control needle valve. Pressure in the rotameter was indicated by a mercury manometer located on the control panel. In order to accomodate the wide variation in air flow rates, the air stream was divided at the downstream control point where both a coarse and a fine control needle valve were installed. The air stream then joined the ammonia stream.

The ammonia was obtained from a commercial gas cylinder. The ammonia stream, as shown in Figures 1 and 3, was reduced to an operating pressure of approximately 10 psig. by a pressure regulator attached to the ammonia cylinder outlet. The ammonia cylinder and pressure regulator are omitted in Figure 3 to prevent obstructing the photograph of the rest of the equipment, but their presence is indicated by a slip of paper near the heat exchanger. A stainless steel, finned-tube heat exchanger was used on the low pressure side of the pressure regulator to ensure that the ammonia would discharge into the column close to room temperature. The ammonia stream was allowed to flow through the inside of the tubes and air from the room constituted the hot fluid on the outside of the tubes from which heat passed into the ammonia. The ammonia passed through one of the calibrated rotameters and the flow rate was controlled in the same manner as for air.

After the air and ammonia streams joined, the resultant stream passed through a series of flow restrictions to ensure complete mixing of the gases. Thermometers were placed in the air, ammonia, and air-ammonia lines. Separate thermometers were used to measure the temperature of the room and of the exit gas from the top of the column.

The air-ammonia mixture was introduced into the column by the gas distributor shown in Figure 7. The distributor was constructed of standard 0.75 inch copper tubing and fittings in the form of a five inch square with three rows of holes all around the tubing on the bottom side. One row of holes was at the bottom of the copper tubing. The two adjacent rows were at angles of thirty degrees around the tube as measured from the bottom row. The holes were 0.0312 inches in diameter and were spaced 0.5 inches apart. The air-ammonia mixture passed through the column to the atmosphere. The excess gases were blown from the building by a large window fan.

A calibrated tank (120 gallons capacity) was used as the water reservoir. Tap water entered the reservoir from a laboratory water line. A recycle line was provided to maintain mixing in the reservoir and to prevent overloading the liquid pump. A drain line was also connected to the reservoir to permit draining and cleaning. The water flowed from the reservoir to a 0.25 horsepower pump by gravity. The water then either entered the liquid flow system or was recycled back to the tank. The water was metered by use of a calibrated rotameter and was controlled by manual operation of a needle valve.

The water entered the liquid distributor shown in Figure 8, which consisted of a five inch diameter, 0.25 inches thick plexiglas plate into which were cemented 25 brass rods 0.5 inches long and 0.25 inches in diameter in the pattern shown in Figure 8. One hole, 0.036 inches in diameter was drilled through the center of each of the rods. The rods were beveled at the upper end to prevent possible clogging of the holes by suspended particles in the water stream. This pattern was designed

to give the same liquid rate per unit cross-sectional area over the whole distributor. A five inch outside diameter plexiglas cylinder with 0.25 inches wall thickness and eight inches high was then cemented to the plate to complete the distributor.

The distributor was centered at the top of the column which was in turn centered on the liquid receiver at the bottom of the column and checked for perpendicular alignment. The liquid receiver was a five inch outside diameter plexiglas cup four inches high which had a wall 0.25 inches thick and was provided with a plastic tubing drain line. The drain line or sample removal line was fitted into the column bottom assembly by means of two grease seals as shown in Figure 6. The flow from the liquid receiver was controlled by a stopcock and adjustable clamp which enabled a constant liquid level to be maintained in the receiver. The drain line was divided to provide a liquid sample removal point and a direct drain line. Temperatures were recorded by thermometers located in the liquid entrance and exit lines. Figure 6 also indicates provisions for draining the column bottom.

A barometer was installed on the control panel to provide a convenient source of barometric data.

A du Nouy Interfacial Tensiometer made by the Central Scientific Company, Chicago, Illinois, was used to measure the surface tension of the absorbing liquid.

Materials.--Tap water was supplied by the Atlanta Water Works, Atlanta, Georgia, and was utilized as the absorbing liquid for this investigation.

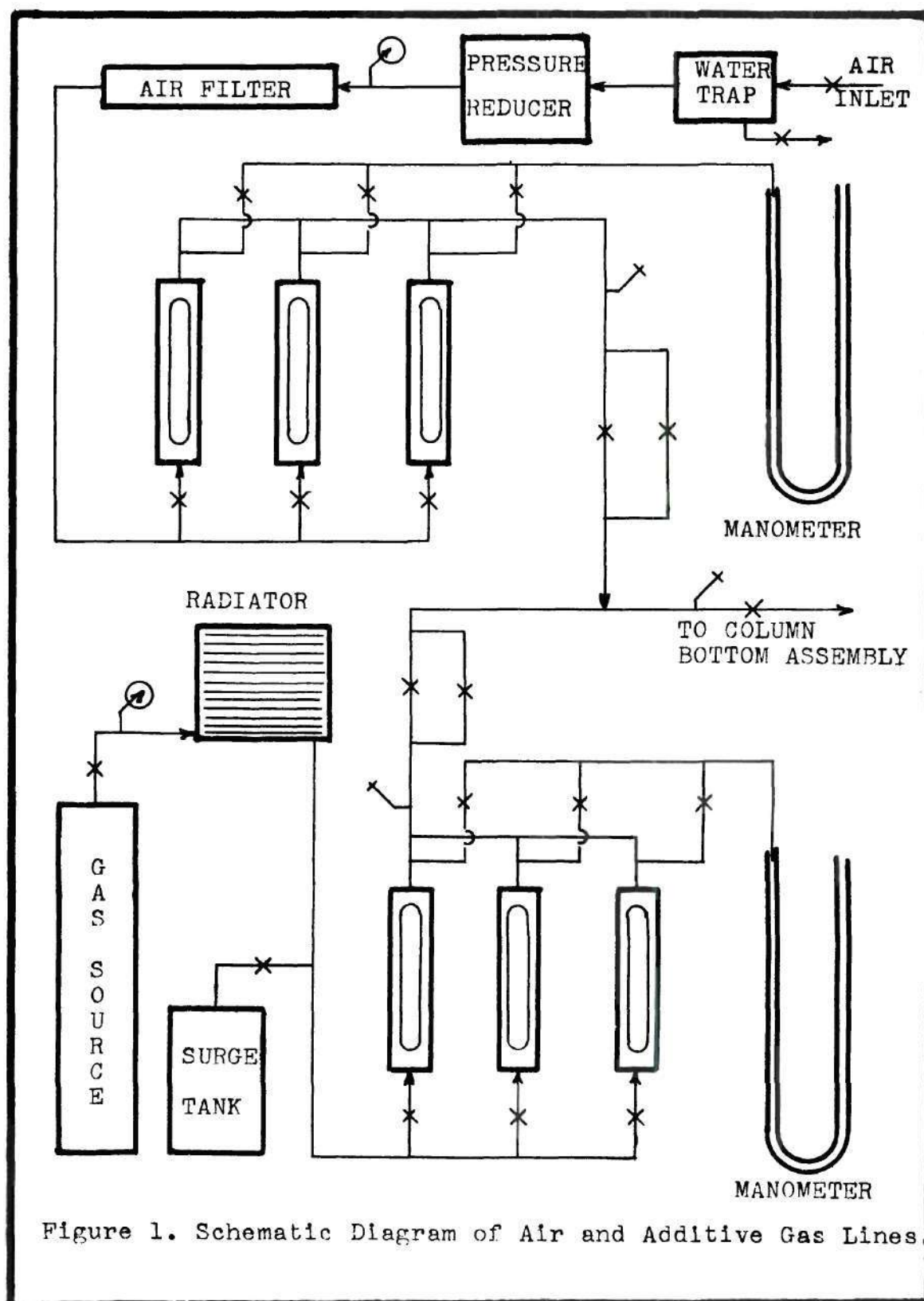
Anhydrous ammonia was obtained in commercial cylinders from Tesco

Chemicals, Inc. of Atlanta, Georgia.

Compressed air was obtained from the central laboratory compressor.

Velocite Oil D, viscosity 100 seconds at 100°F, was furnished by the Standard Oil Company of Kentucky distributor in Atlanta, Georgia. This oil was used as the screening film for the liquid in the drop receiver at the bottom of the column.

The surface active agent, sodium oleate, was furnished by the J. T. Baker Chemical Company of Phillipsburg, New Jersey.



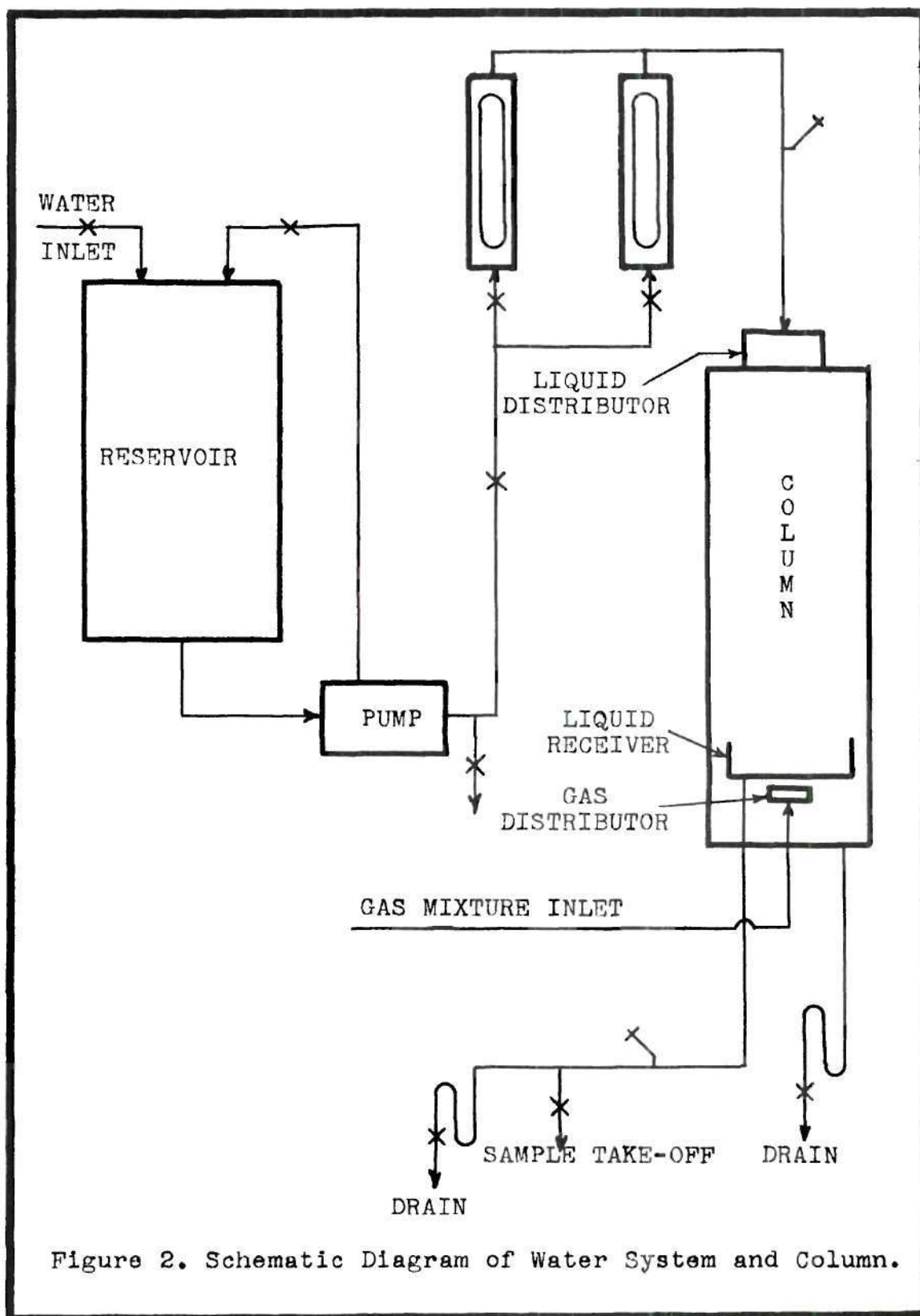


Figure 2. Schematic Diagram of Water System and Column.

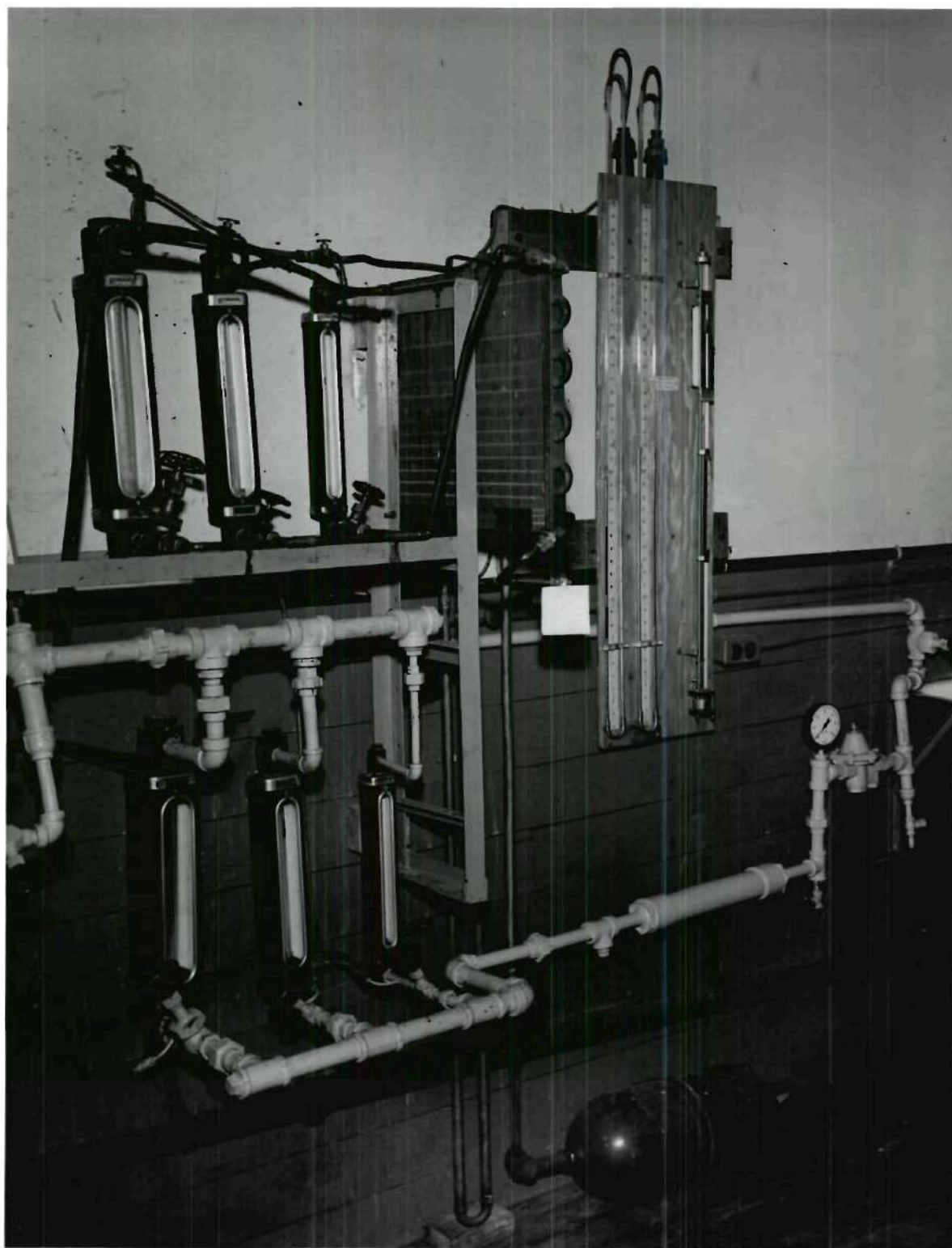


Figure 3. Photograph of Air and Gas Lines.

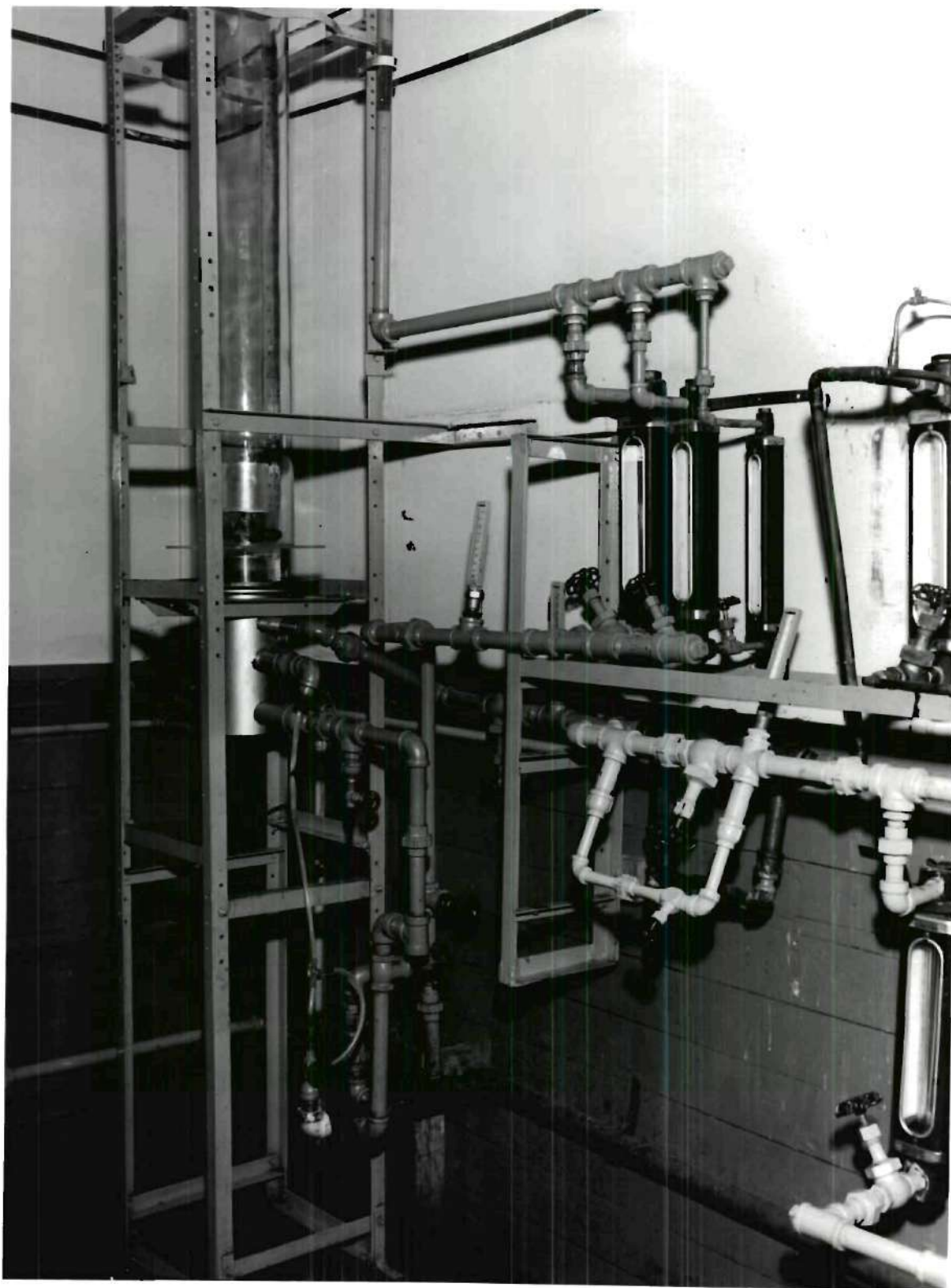


Figure 4. Photograph of Water System and Column Assembly.

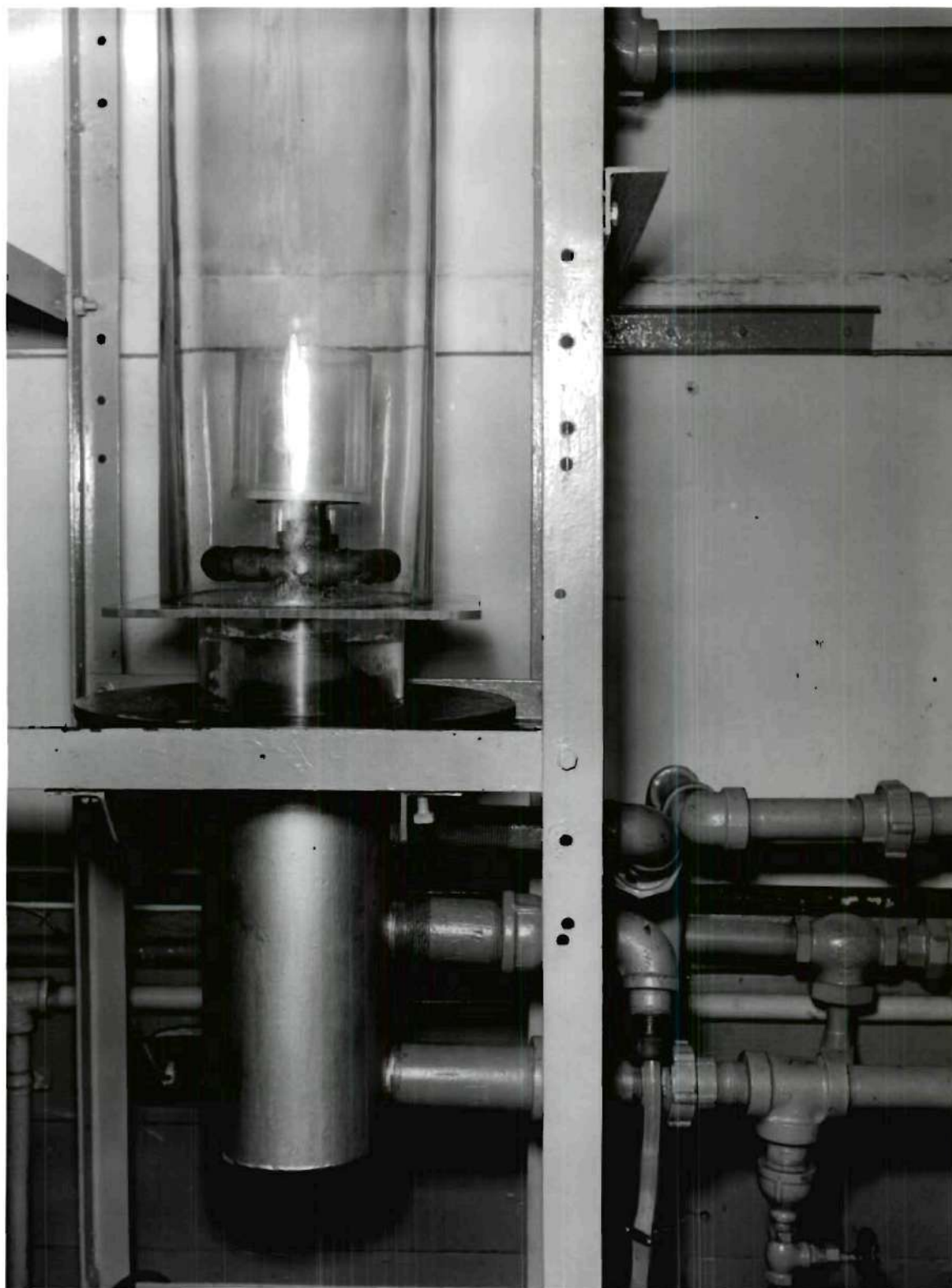
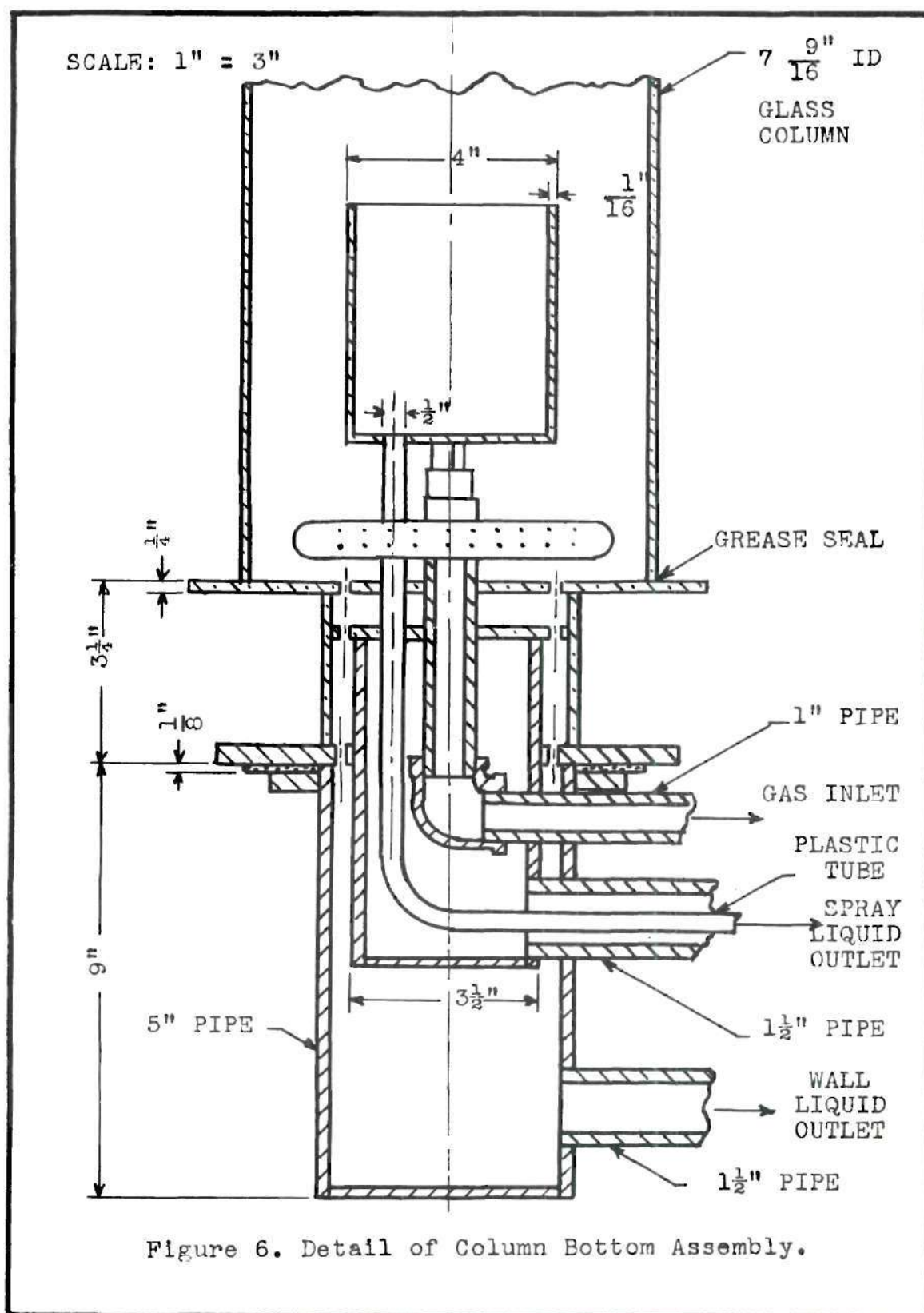


Figure 5. Photograph of Column Bottom Assembly.



SCALE: 1" = 1"

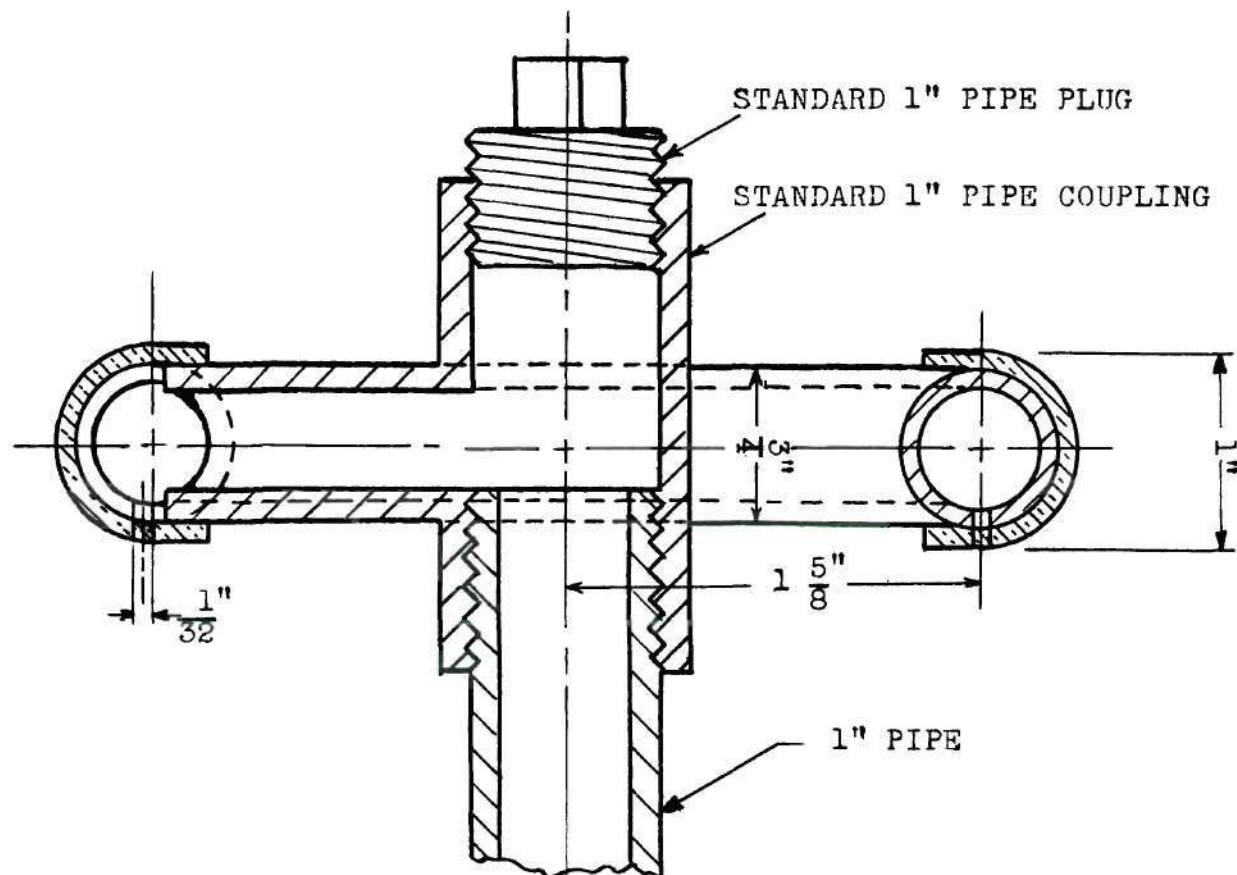
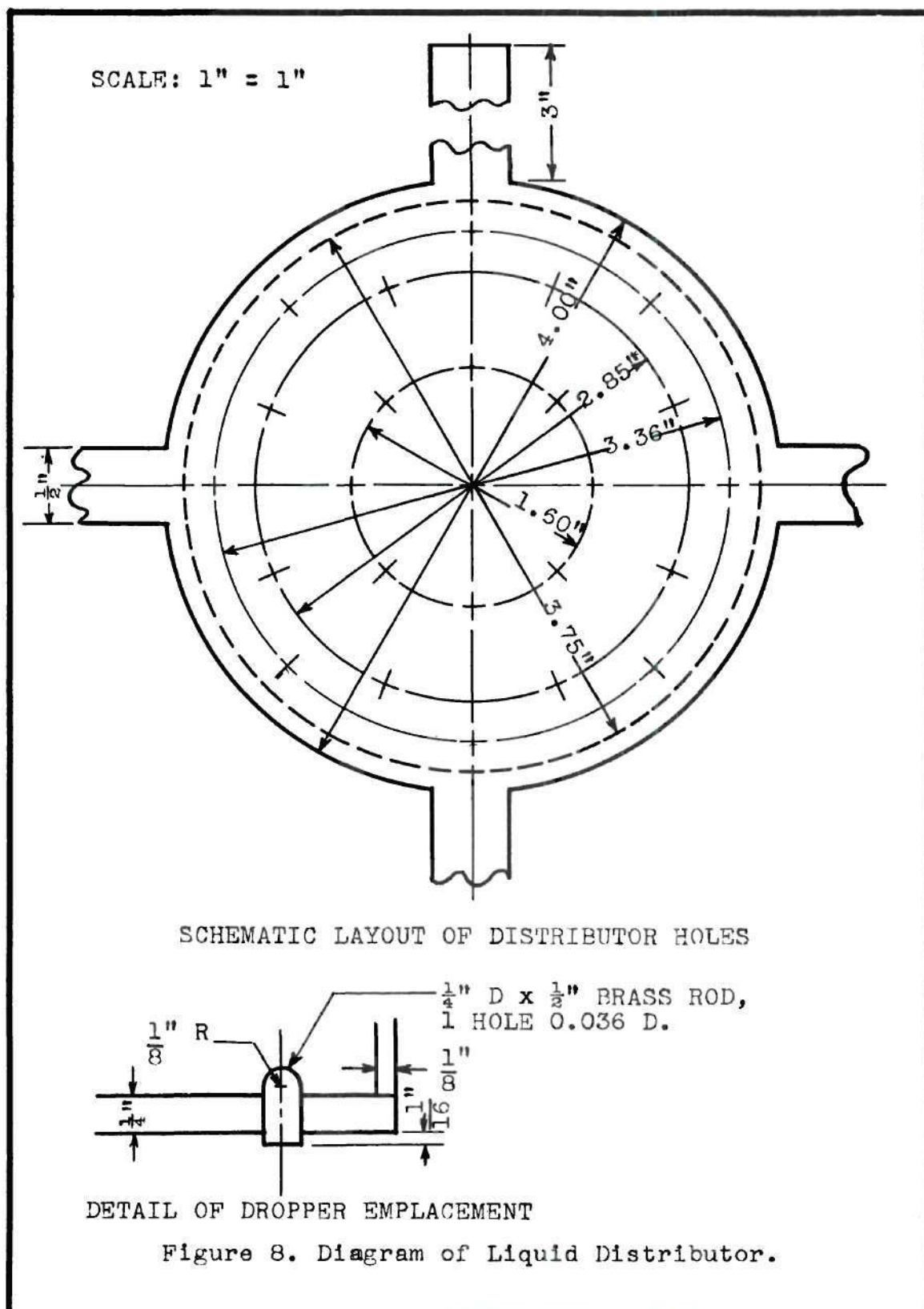


Figure 7. Detail Diagram of Gas Distributor.



CHAPTER III

EXPERIMENTAL PROCEDURES

General.--Since in the course of this investigation the same type of experimental data for all the systems was to be collected, a general procedure common to all runs was established.

The liquid rate for all runs was held constant at 0.5 pounds per minute. Consequently, at the beginning of a series of runs, the liquid head in the distributor was so adjusted that the fixed amount flowed through the distributor and into the column. The gas rate and gas composition to be investigated were selected and the control equipment was adjusted until the column was operating in a steady state. The equipment was allowed to operate about 15 minutes after constant flow rates were obtained to ensure complete flushing of the column and to ensure reasonably constant operation before data was obtained. During this period a volume of Velocite Oil D was introduced into the liquid receiver cup in order to maintain a 0.5 inch oil layer on the aqueous liquid surface. The purpose of this layer was to isolate the liquid under investigation from the surrounding atmosphere of ammonia as soon as the free fall period of the drops was completed. A series of top and bottom samples were taken and analyzed. When the results were constant, the values were recorded. During the equilibrium period, all thermometers, rotameters, and manometers were constantly monitored to ensure constant flow conditions.

Immediately following a run, the gas rate was changed, maintaining the same gas composition and liquid flow rate, and the cycle outlined above was repeated. This procedure was followed until four gas rates were examined for each gas composition. Three gas compositions were employed for each liquid composition.

If the experimental run included the use of the surface active agent, the sodium oleate was added to the water in the reservoir and was recycled for several hours to ensure a homogeneous liquid phase with constant surface tension. A series of runs were made using plain tap water as a basis for comparison with runs in which an agent was present.

Comments on the general procedure.--Further discussion is in order on some details of operation not described in the general outline of the experimental procedure.

Constant regulation of the downstream pressure control needle valve governing the air flow was necessary due to fluctuations in supply pressure. As mentioned in Chapter II, the gas rotameters were calibrated at 10 psig. and even slight variations in pressure in these rotameters could cause considerable deviation from the desired flow. This difficulty was not encountered in the ammonia supply due to the constant supply pressure.

The liquid reservoir was drained and scrubbed after the experimental runs on a specific concentration of the surface active agent had been completed. Thorough flushing of the system was performed periodically to prevent fouling of the rotameters by any entrained rust

particles or other foreign matter.

Analytical procedures.--The top and bottom samples were transferred to clean stoppered flasks and were titrated as soon as possible with standardized solutions of hydrochloric acid using phenolphthalein as the indicator. After the titrations were completed, the flasks were thoroughly washed with cleaning solution and were dried in a moisture oven. They were then stoppered and stored for future use.

Carefully prepared solutions of potassium hydrogen phthalate and sodium hydroxide were used in the standardization of the hydrochloric acid solutions. These hydrochloric acid solutions were restandardized before and after each series of experimental runs.

The surface tension of the liquid was determined before and during each series of runs through the use of a du Nouy Interfacial Tensiometer. This apparatus was calibrated with distilled water and with weights of known mass. The tensiometer was recalibrated before each of the determinations of surface tension. Figure 11 in Appendix IV shows the relation between surface tension and the concentration of sodium oleate in water.

CHAPTER IV

METHOD OF CALCULATION

Sherwood and Pigford (20) schematically represent an absorption column in a manner similar to Figure 9.

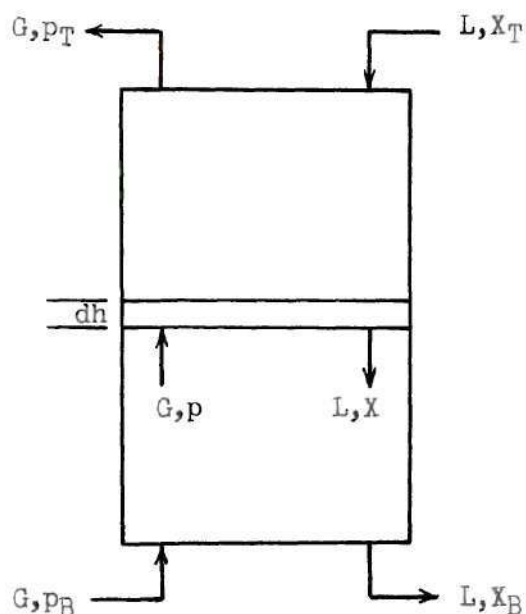


Figure 9. Schematic Diagram of a Countercurrent Absorption Column.

In Figure 9, G and L are respectively the amount of gas and liquid flowing through the column, X is the weight ratio of the solute to the solvent in the liquid stream, p is the partial pressure of the solute gas in the gas stream and the subscripts B and T represent the bottom and the top of the column respectively.

(20) Sherwood, T. K., and R. L. Pigford, Absorption and Extraction. New York: McGraw-Hill Book Company, Inc., 1952, p. 117.

By a material balance,

$$c L (X_B - X_T) = G (p_B - p_T) \quad (2)$$

where c is a conversion factor to convert from weight ratio to equivalent partial pressures.

If N_A is the amount of solute absorbed per unit area per unit time, a material balance covering a differential section of the column can be written as:

$$N_A a dV = K_G a (p - p_e) dV \quad (3)$$

where: a is the effective area per unit volume

V is the volume of the column

K_G is the over-all mass transfer coefficient (gas film controlling)

p is the partial pressure of solute in the main gas stream

p_e is the pressure of solute in equilibrium with the concentration of the solute in the main body of the liquid

Since the amount of solute absorbed is the same as the material lost by the gas phase, the following equation may be written:

$$N_A = K_G (p - p_e) \quad (4)$$

where $(p - p_e)$ is the driving force in pressure units which causes the solute to diffuse through the interface.

To solve for the over-all mass transfer coefficient in equation (4), an average driving force must be used which applies for the entire height of the column. When the equilibrium curve is essentially a straight line, it can be shown that the logarithmic mean of the terminal

pressures is a theoretically correct average. This logarithmic mean driving force can be expressed by the equation:

$$(p - p_e)_{lm.} = \frac{(p - p_e)_B - (p - p_e)_T}{\ln \left[\frac{(p - p_e)_B}{(p - p_e)_T} \right]} \quad (5)$$

In this investigation the amount of ammonia absorbed was negligible as compared to the amount in the main gas stream, therefore the partial pressure in the main gas stream was essentially constant throughout the height of the column. Using this fact, equation (5) can be reduced to:

$$(p - p_e)_{lm.} = \frac{p_{eT} - p_{eB}}{\ln \left[\frac{(p - p_e)_B}{(p - p_e)_T} \right]} = \frac{p_{eB} - p_{eT}}{\ln \left[\frac{(p - p_e)_T}{(p - p_e)_B} \right]} \quad (6)$$

By the substitution of equation (6) in equation (4) and solving for the over-all mass transfer coefficient the following equation may be obtained:

$$K_G = \frac{N_A}{(p - p_e)_{lm.}} = \frac{N_A}{\frac{(p - p_e)_B - (p - p_e)_T}{\ln \left[\frac{(p - p_e)_B}{(p - p_e)_T} \right]}} \quad (7)$$

CHAPTER V

RESULTS AND DISCUSSION

The results of the experimental runs when shown in graphical form lie along a straight line if the logarithm of the over-all gas film coefficient is plotted against the logarithm of the gas rate. This correlation appears in Figure 10 in Appendix III. The results of this investigation can be expressed algebraically by means of the following empirical equation:

$$K_G = 0.76 u^{0.258} \quad (8)$$

where: K_G is the over-all gas film coefficient

u is the gas rate expressed in cubic feet per minute
at one atmosphere pressure and 80 degrees Fahrenheit

The values of the over-all gas film coefficient were determined using plain tap water and 0.05, 0.02, and 0.01 weight per cent sodium oleate solution. For each of the forementioned solutions, the ammonia-air compositions varied from one to five per cent and the mixture flow rates varied from 0.147×10^{-3} to 2.058×10^{-3} pound moles ammonia per minute. The data for the determination of these values are presented in tabulated form in Tables 1 through 4 inclusive in Appendix I.

The experimental data for the investigation exhibited very good agreement. A maximum deviation of only five per cent was observed in the actual values of the over-all gas film coefficient from those calculated from the empirical equation.

It is of particular significance to note that when the surface active agent was present, there was no appreciable change in the value of the over-all gas film coefficient from the values that had been obtained when using pure water as the absorbent under the same conditions.

There was increased absorption of the ammonia when the 0.02 and 0.05 weight per cent concentrations of sodium oleate were used. However, the decrease in surface tension caused by the addition of the agent decreased the size of the liquid droplets and correspondingly increased the surface area per unit volume of liquid flowing. This increase in surface area cancelled out the increase in ammonia absorbed and the pound moles absorbed per square foot per hour remained essentially constant for any particular gas rate and composition regardless of the concentration of the agent in the liquid.

The results of this investigation agree with the postulates of Rennolds (9) and Sherwood and his co-workers (10,11,12) who contend that the absorption rate is not effected appreciably by the surface active agent in the liquid phase when the gas film is controlling.

(9) Rennolds, op. cit.

(10) Sherwood and Holloway, op. cit., p. 611.

(11) Sherwood and Jenny, op. cit., p. 265.

(12) Sherwood and Holloway, op. cit., p. 765.

CHAPTER VI

CONCLUSIONS

From the results of the investigation, the following conclusions were drawn:

1. The presence of sodium oleate in the liquid phase in no way affected the over-all gas film coefficient.
2. The decrease in surface tension obtained by use of the sodium oleate was responsible for increased absorption of the ammonia, but this effect was due to the increase in surface area.

CHAPTER VII

RECOMMENDATIONS

As a result of this study of the effect of surface active agents upon the over-all mass transfer coefficient, the following recommendations are made for a more general study of the effects of surface active agents:

1. It is recommended that future investigators utilize some system where the liquid droplets will have a longer exposure time to the gas and a period of formation away from the atmosphere in which the gas to be absorbed is present.

2. It is recommended that for more general results, future investigators use several types of surface active agents and several additive gases to be absorbed encompassing the entire range of non-ionic to ionic agents and slightly soluble to very soluble gases.

A P P E N D I X

APPENDIX I

EXPERIMENTAL DATA¹

Table 1. Absorption Data for Tap Water

Run No.	Ammonia Conc.	Gas Rate	Ammonia Absorbed x 10 ⁵		Over-all Gas Film Coefficient	Temp.
			lb. moles hr.	lb. moles hr. - ft. ²		
9	1	23.80	28.14	10.73	1.68	86
10		17.90	26.90	10.26	1.61	
11		11.90	24.66	9.40	1.46	
12		6.00	20.34	7.75	1.20	
5	3	19.83	76.40	29.13	1.65	85
6		13.47	69.49	26.50	1.50	
7		7.93	60.90	23.22	1.30	
8		2.00	43.01	16.40	0.91	
1	5	16.66	119.85	45.70	1.57	83
2		11.90	110.31	42.06	1.44	
3		7.14	97.21	37.06	1.26	
4		2.38	74.33	28.34	0.96	

Atm. pressure--741 mm. Mercury
Drop rate--100 drops per minute

¹The ammonia concentrations are tabulated in mole per cent.
The gas rates are expressed in cubic feet per minute of air-ammonia mixture.
The over-all gas film coefficients are expressed in pound moles per hour per square foot per atmosphere.
The temperatures are expressed in degrees Fahrenheit.

Table 2. Absorption Data for 0.05 Weight
Per Cent Sodium Oleate Solution

Run No.	Ammonia Conc.	Gas Rate	Ammonia Absorbed $\times 10^5$		Over-all Gas Film Coefficient	Temp.
			$\frac{\text{lb. moles}}{\text{hr.}}$	$\frac{\text{lb. moles}}{\text{hr.} - \text{ft.}^2}$		
45	1	23.80	38.04	11.27	1.78	83
46		17.90	33.43	9.91	1.56	
47		11.90	30.81	9.13	1.43	
48		6.00	25.08	7.43	1.15	
41	3	19.83	94.58	28.03	1.59	83
42		13.47	92.58	27.44	1.56	
43		7.93	74.95	22.21	1.25	
44		2.00	54.76	16.23	0.90	
37	5	16.66	159.50	47.27	1.64	83
38		11.90	133.72	39.63	1.36	
39		7.14	130.08	38.55	1.32	
40		2.38	94.87	28.12	0.95	

Atm. pressure--741 mm. Mercury
Drop rate--213 drops per minute

Table 3. Absorption Data for 0.02 Weight
Per Cent Sodium Oleate Solution

Run No.	Ammonia Conc.	Gas Rate	Ammonia Absorbed x 10 ⁵		Over-all Gas Film Coefficient	Temp.
			<u>lb. moles</u> <u>hr.</u>	<u>lb. moles</u> <u>hr. - ft.²</u>		
33	1	23.80	30.40	11.06	1.74	83
34		17.90	27.83	10.13	1.59	
35		11.90	25.15	9.15	1.43	
36		6.00	22.00	8.01	1.24	
29	3	19.83	78.28	28.49	1.61	83
30		13.47	74.42	27.09	1.53	
31		7.93	64.12	23.34	1.31	
32		2.00	44.65	16.25	0.90	
25	5	16.66	123.95	45.11	1.56	83
26		11.90	114.96	41.84	1.44	
27		7.14	102.09	37.16	1.27	
28		2.38	77.02	28.03	0.95	

Atm. pressure--742 mm. Mercury

Drop rate--115 drops per minute

Table 4. Absorption Data for 0.01 Weight
Per Cent Sodium Oleate Solution

Run No.	Ammonia Conc.	Gas Rate	Ammonia Absorbed x 10 ⁵		Over-all Gas Film Coefficient	Temp.
			<u>lb. moles</u> hr.	<u>lb. moles</u> hr. - ft. ²		
21	1	23.80	27.91	10.64	1.67	85
22		17.90	27.07	10.32	1.61	
23		11.90	24.64	9.39	1.46	
24		6.00	20.37	7.77	1.20	
17	3	19.83	75.78	28.89	1.64	85
18		13.47	70.17	26.75	1.51	
19		7.93	60.93	23.23	1.30	
20		2.00	42.06	16.04	0.89	
13	5	16.66	120.14	45.81	1.58	85
14		11.90	108.61	41.41	1.42	
15		7.14	97.85	37.31	1.28	
16		2.38	74.11	28.26	0.96	

Atm. pressure--740mm. Mercury
Drop rate--100 drops per minute

APPENDIX II

SAMPLE CALCULATION

The amount of ammonia absorbed.---To determine the amount of ammonia absorbed, the top and bottom samples were titrated with standardized solutions of hydrochloric acid. To simplify the calculations, all titrations were adjusted from the actual volumes and normalities of the acid solution to an equivalent volume of 0.0500 normal acid. Using the strength of the ammonia solutions of the top and bottom samples, the amount of ammonia absorbed during the free fall period of the drops can be calculated. For example:

Run #3

Pressure in mm. mercury	741
Drops per hole per minute	100
Temperature in degrees Fahrenheit	83
Sample volume in ml.	100
Normality of HCl solution	0.0500
Volume of HCl solution to neutralize bottom sample in ml.	114.30
Volume of HCl solution to neutralize top sample in ml.	49.49

By the use of a conversion factor, it was found that 97.21×10^{-5} pound moles ammonia were absorbed per hour during the free fall period of the drops.

To calculate N_A , pound moles ammonia absorbed per hour per square foot, the drop count average must be used to calculate the effective area. Using the flow rate of the liquid, the density of the liquid, and the drop rate multiplied by 25 (the number of holes in the distributor),

the following expression was obtained for the total surface area per minute:

$$A = 0.566 (R)^{1/3} \quad (9)$$

where: A is the total surface area per minute

R is the drop rate in drops per minute per hole

To obtain the effective area equation (9) must be multiplied by 0.00792, the drop fall time in minutes. The resulting equation is:

$$a = 0.00792 A = 0.00448 (R)^{1/3} \quad (10)$$

where: a is the effective area

For run #3, $R = 100$ and $a = 0.0208$. Thus 97.21×10^{-5} is divided by 0.0208 and $N_A = 46.74 \times 10^{-3}$.

Logarithmic mean driving force.---The calculation of the log mean driving force requires vapor pressure data. A graph was prepared by plotting the vapor pressure against the concentration of ammonia in solution. From the data for run #3, the concentrations of the top and bottom samples could be found and converted to the proper units to conform with the graph. Equivalent partial pressures could be determined from the graph and substituted into equation (6), Chapter IV:

$$(p - p_e)_{lm.} = \frac{p_{eB} - p_{eT}}{\ln \left[\frac{(p - p_e)_T}{(p - p_e)_B} \right]} \quad (11)$$

Thus for run #3, the log mean driving force was 37.03×10^{-3} atmospheres.

Over-all gas film coefficient.--To obtain the over-all gas film coefficient, equation (7), Chapter IV, was used. The Value for K_G for run #3 was:

$$K_G = \frac{N_A}{(p - p_e)_{lm.}} = \frac{46.74 \times 10^{-3}}{37.03 \times 10^{-3}}$$

$$K_G = 1.26 \frac{\text{lb. moles}}{\text{hr} - \text{ft}^2 - \text{atm}}$$

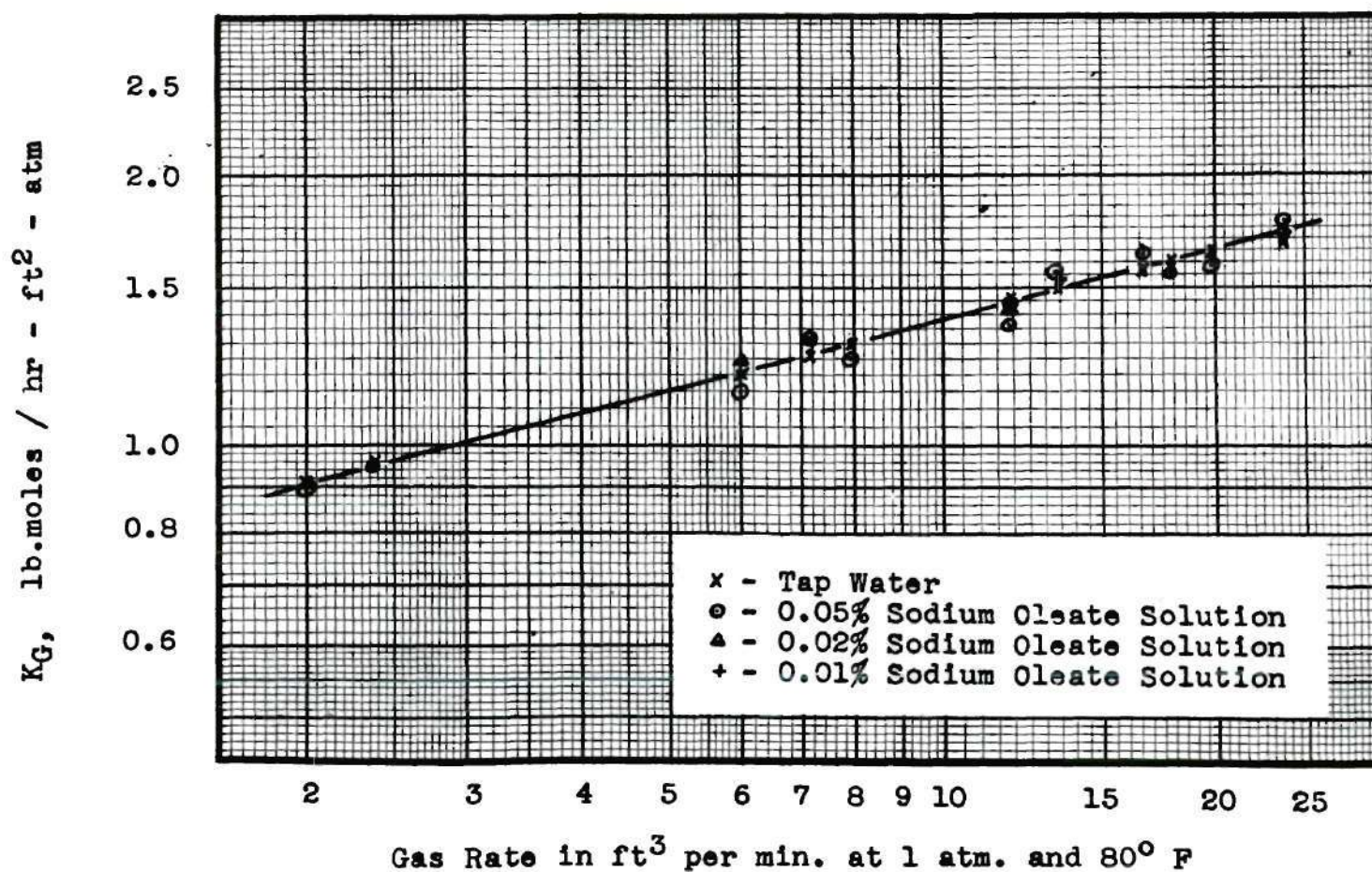


Figure 10. Over-all Gas Film Coefficient - Gas Rate Curve.

APPENDIX IV

SURFACE TENSION DATA IN GRAPHICAL FORM

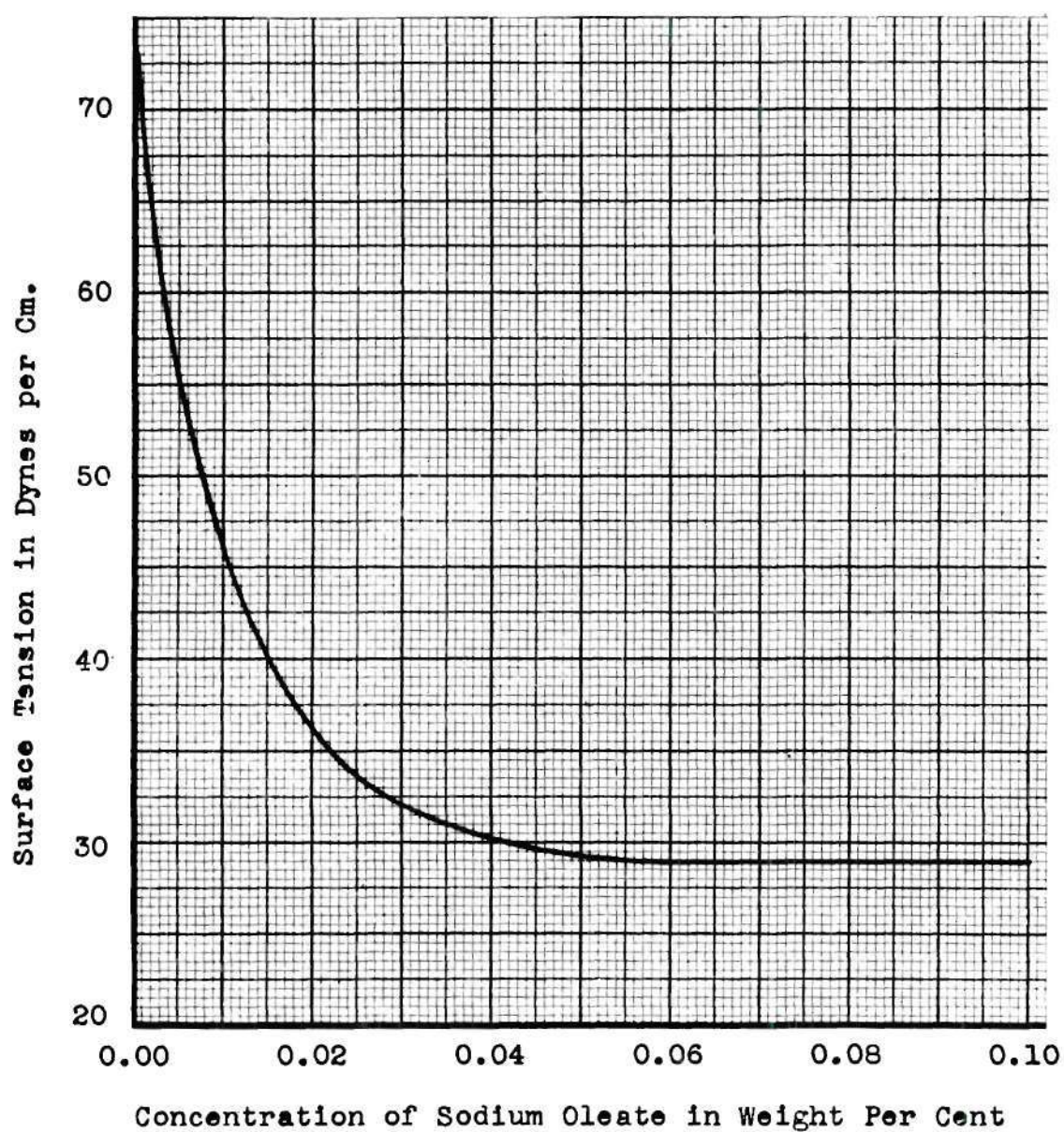


Figure 11. Surface Tension Curve of Sodium Oleate

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